Chemical Adsorption of Nitrogen Dioxide with an Activated Carbon Adsorption System

Mei-Ling Fang[1], Ming-Shean Chou[1], Cheng-Yu Chang[1], Hsiao-Yu Chang[1*], Chih-Hsiang Chen[2,3], Sheng-Lun Lin[4,5,6*], Yen-Kung Hsieh[7]

[1] *Institute of Environmental Engineering, National Sun Yat-sen University, Kaohsiung 80424, Taiwan*
[2] *Department of Finance, Ming Chuan University, Taipei 11103, Taiwan*
[3] *School of Software and Microelectronics, Peking University, Beijing 102600, China*
[4] *Department of Civil Engineering and Geomatics, Cheng Shiu University, Kaohsiung 83347, Taiwan*
[5] *Center for Environmental Toxin and Emerging-Contaminant Research, Cheng Shiu University, Kaohsiung 83347, Taiwan*
[6] *Super Micro Mass Research and Technology Center, Cheng Shiu University, Kaohsiung 83347, Taiwan*
[7] *Ocean Affairs Council, Kaohsiung 80661, Taiwan*

ABSTRACT

Nitrogen dioxide (NO_2) is a pollutant that directly harm the human respiratory system, lead to inflammation, as well as to form the secondary aerosol pollutants. The main NO_2 sources, combustion or thermal processes, were well controlled. However, the metal etching operation in semiconductor industry emits flue gases with reddish-brown NO_2 fume that leads to visibility reduction, acidic odor, as well as negative effects on human health. In this study, a stream of flue gases with low NO_2 (230 ± 10 ppm) and NO (50 ppm) concentrations were conducted to pass through an activated carbon-packed fixed bed for analyzing the adsorptive conversion behavior of NO_2 by the activated carbon (AC) at room temperature. The repeated adsorption test was carried out by washing the regenerated waste carbon with a caustic solution and water and drying. Results propose that at the beginning of adsorption, nitrogen dioxide combined with carbon to form NO and desorbed from carbon surface. The net adsorptive conversion removal capacity of NO_2 by the virgin AC and regenerated AC was 224 and 155 mg g^{-1} AC, respectively. Regeneration restored around 70–75% of effective surface area, pore volume, and adsorptive conversion capacity of the virgin AC. Leached caustic solution obtained from the carbon regeneration contained only nitrate and the phenomena indicates the adsorbed -$C_2(ONO_2)$ hydrolyzed following the Eq. (2) -$C_2(ONO_2)$ + H_2O → 3 -C* + -C(O) + 2 HNO_3, where -C* denotes active site on the carbon surface.

Keywords: Activated carbon; Nitrogen dioxide; Adsorption; Air pollution control.

INTRODUCTION

Nitrogen dioxide is an important pollutant in the air index. The exhaust gas generated by the metal etching operation in the TFT process has a reddish-brown color (yellow when diluted). The NO_2 smoke has photochemical reactivity, which may cause acidic odor, cardiovascular effects, lung cancer, and negative health effects. (Wu and Chou, 2014; Du *et al.*, 2017; Fang *et al.*, 2017; Jiang *et al.*, 2017; Xu *et al.*, 2017; Zhang *et al.*, 2017; Wang *et al.*, 2018).

Techniques most commonly used to eliminate NO_2 gas include selective non-catalytic reduction (SNCR), chemical scrubbing, and selective catalytic reduction (SCR). SCR and SNCR operate at gas temperatures in the range of 270–400°C and 900–1000°C, respectively, indicating they would be both better operated under high-temperature flue gas condition (Shen and Rochelle, 1998; Chen *et al.*, 2002; Curtin, 2005; Gao *et al.*, 2009; Chen *et al.*, 2011; Gao *et al.*, 2011; Gao *et al.*, 2012; Wu and Chou, 2014; Huang *et al.*, 2017; Liu *et al.*, 2017; Chen *et al.*, 2018). The most suitable method for removing NO_2 and mixed acids, e.g., nitric and phosphoric, is wet scrubbing with sodium sulfide and caustic soda by the following equation: 8 NO_2 + NaSH + 9 NaOH → 8 $NaNO_2$ + Na_2SO_4 + 5 H_2O. They are commonly used in an aluminum etching processes for producing thin film transistors-liquid crystal displayers. Unfortunately, the odor of hydrogen sulfide would further be emitted from the

---
* Corresponding author.
  Tel.: 886 7735 8800 ext. 2605
  E-mail address: cbmsgml@gmail.com
** Corresponding author.
  Tel.: 886 7525 4428
  E-mail address: d9033803@student.nsysu.edu.tw

effluent of the scrubber and become a secondary pollution (Wu and Chou, 2014).

Gao *et al.* (2011) reported reactive adsorption of NO to NO_2 at 50°C. It was then observed that NO_2 was adsorbed and reduced to NO, when the AC was exposed to NO_2. The study showed that no net removal of NO_x (NO and NO_2) was observed when NO_2 was adsorbed and NO desorbed at 50°C. However, this study indicates that AC micropores form a decomposition reaction site that is released together with -C(ONO_2)-C-NO and NO. (Gao *et al.*, 2011).

The processes of NO_2 adsorption-reduction on pitch-based ACF (activated carbon fiber) was reported with the controlled conditions of NO_2 (250–1000 ppm) and O_2 (0–10%) in the tested gaseous mixture at 30–70°C (Shirahama *et al.*, 2002). ACFs shows rapid NO_2 conversion and reduction at 30°C, while the NO was continuously and steadily produced before the approaching of NO_2 adsorption limit. The higher reaction temperature (70°C) was found to decrease the adsorption rate in a steady-state test and shorten the operation period before the breakthrough of NO_2. In addition to this, NO_x adsorbed on ACF were oxidized from NO_2 to NO_3. This result points out that there are two pathways of NO_2 adsorptions. One of them weakly adsorbs NO_2 and terminate the adsorption and reduction when the active sites were saturated. The adsorbed NO_3 generates NO_2 and NO, following the reactions of -C(ONO_2) → -C-(NO_2) + -CO and -C(ONO_2) → -C-NO + -CO_2 under heating process. The other strongly adsorption mechanism were approached by the reaction as 2-C-NO_2 → -C-NO + -C(ONO_2). The adsorbed NO (-C-NO) was decomposed and released from the carbon surface and leaves NO_3 bound with the surface of AC. One or two oxygen atom(s) were leaved on the AC surface and simultaneously evolve as CO and CO_2, which further recovered the ability of NO_2 adsorption (Shirahama *et al.*, 2002).

Additionally, Zhang *et al.* (2008) indicated that the estimated NO_2 adsorption capacity of activated carbon was about 70 g kg^{-1} at 25°C, before it released NO_2 from saturated carbon bed. There was no NO emission during the first 30-minute operation. Depending on the surface conditions, some of NO formed by the NO_2 conversion was adsorbed on the activated carbon surface, when the other was released into the exhaust gas. During thermal desorption, O_2, NO and a small amount of CO and CO_2 were released at the temperatures < 150°C. (Zhang *et al.*, 2008).

In some small metal etching processes, a limited flow of exhaust gas emitted only NO_2. activated carbon can be used to convert NO_2 to NO, eliminating the color issues before emission. AC can also be used to purify indoor ambient air to protect people from long-term exposure with low NO_2 concentrations. The US. EPA list 0.053 ppm as the average 24-hour limit for NO_2 in outdoor air (U.S. Environmental Protection Agency, 1987). The full or partially saturated AC could be regenerated by a caustic solution washing process. The processes may be simple in term of their treatment system and operation steps; however, their performance and economical information are still limited. Görgülü *et al.* (2018) stated that the nitrogen dioxide concentration existing in the environment can be harmful, in particular for asthmatics and it also has the potential to bring about other serious diseases. They observed the nitrogen dioxide adsorption on the active carbon for varying air temperatures, gas concentrations and air relative humidity. They have used parameters between 1 ppm and 30 ppm (for NO_2 concentration), 23°C and 33°C (for air temperature), 30% and 90% (for air relative humidity). Results show that the humidity has not a remarkable effect on the adsorption of NO; however, increasing relative humidity causes to a decrease in the capacity of the activated carbon for NO adsorption.

The current research focuses on the performance of an activated carbon bed for NO_2 adsorption and the regeneration technique of saturated carbon with a caustic solution. The washed solution was analyzed to ascertain if the adsorbed NO_2 was converted to nitrite and/or nitrate ions.

METHODS AND MATERIALS

The experimental setup consisted of a column packed with granular activated carbon (AC) and a NO_x-containing gas preparation and delivery system, as demonstrated in Fig. 1. The AC-packed column had an inner diameter of 1.0 cm and packed with crushed and screened AC for adsorption tests. The tested virgin activated carbon (ACRO-460) was supplied by ACRO Chemical Co., Taiwan. Table 1 shows the specifics some of the characteristics of the original AC received. The AC was crushed, ground and screened to get a sample of fine grains with sizes in 0.84–1.00 mm. Before packing, the AC sample was conditioned in a desiccator for around 24 hours at 25 ± 2°C to get an equilibrium moisture content of about 5%. The sample was then weighted and packed into the column to a definite height for the adsorption test.

The operation conditions for adsorption tests were designed as shown in Table 2. During the first test, the effluent gas samples were analyzed half an hour for NO and NO_2. The AC were eventually saturated by NO_2, while the NO_2 level in the effluent gas remained equal to the inlet port. After the saturation of NO_2, the AC was immersed in 200 mL of an alkaline aqueous solution adjusted to pH 10 using NaOH and stirred for 14 hours to leach the adsorbed nitrate and/or nitrite. The leached AC was then filtered by a suction pump and the filtrate stored for chemical analysis. The AC was then soaked in 200 mL pure water and stirred for 2 hours to leach out the residual nitrite and/or nitrate. The 2nd-leached AC (the regenerated AC) was again filtered and the filtrate stored for chemical analysis. The regenerated AC was conditioned in the desiccator for 24 hours before being packed into the column. Because some AC was taken for analysis, mass of the AC for the 2nd adsorption test was less than the previous one (Table 2). The 2nd adsorption test lasted for 630 minutes. The virgin, exhausted virgin, regenerated, and exhausted regenerated carbon were analyzed for their surface properties, pore volume, and adsorbed oxygen contents.

A flue gas analyzer (Testo-340, Testo/Germany) was employed to determine the concentrations of NO and NO_2 in gas samples. The analyzer has an accuracy of ±5%, according to the specifications supplied by the manufacturer. An ion chromatography (ICS-900, Dionex/USA) was utilized to quantify the levels of nitrite and nitrate in the filtrates obtained from the first regeneration and washing eluent.
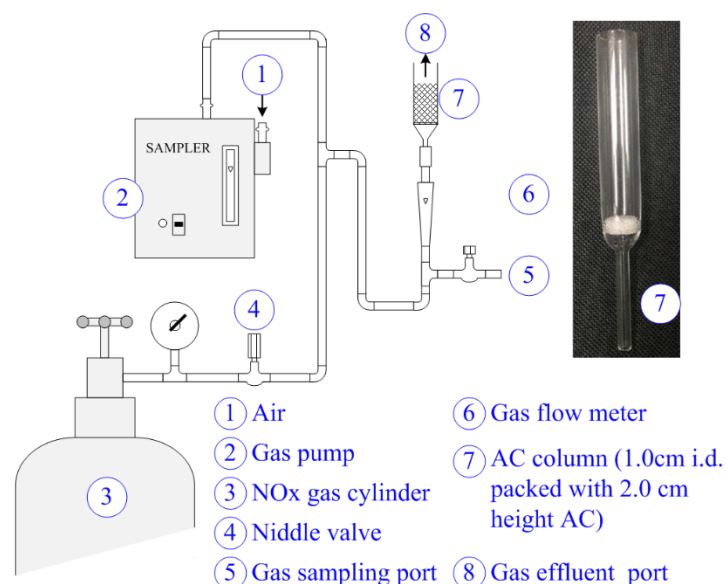
①Air
②Gas pump
③NOx gas cylinder
④Niddle valve
⑤Gas sampling port
⑥Gas flow meter
⑦AC column (1.0cm i.d. packed with 2.0 cm height AC)
⑧Gas effluent port

Fig. 1. Schematics of the experimental system.

Table 1. Some characteristics of the experimental AC as received.

Items	Characteristics
Appearance	Cylindrical
Bulk density	0.4–0.5 g mL^{-1}
Moisture	< 5%
Iodine value	850 mg g^{-1}

Table 2. Influent gas to the AC column and the operating conditions.

Item	Parameters	
Influent gas	NO$_2$	230 ± 10 ppm
	NO	50 ppm
	NO$_x$ (NO$_2$ + NO)	280 ± 10 ppm
Influent gas flow rate	0.6 L min^{-1}	
Operating temperature	25°C	
Inner diameter of AC column	1.00 cm	
Superficial velocity for the gas flowing through the column cross-sectional area	0.127 m s^{-1} @25°C	
Packed height and mass of virgin AC	2.00 cm/0.75 g	
Packed height and mass of regenerated AC	1.70 cm/0.69 g	

The pH of the filtrates was measured by a pH meter (pH 526, WTW/Germany). The instrument used to analyze the surface area and pore volume of the AC sample was a BET surface analyzer (ASAP 2020 Accelerated Surface Area and Porosimetry System, Micromeritics Instrument Co., USA).

RESULTS AND DISCUSSION

NO$_2$ Adsorptive Removal Breakthrough Curves

Fig. 2(A) shows NO, NO$_2$ and NO$_x$ (NO + NO$_2$) concentrations of the gas influent to and effluent from the bed packed with the virgin AC as a function of time. During the initial 210 min, there was less than 10 ppm NO$_2$ emitted from the bed, indicating the removal efficiency of NO$_2$ approached over 90% (as shown in Fig. 3). However, the effluent gas contained 102–196 ppm in addition to the influent

50 ppm of NO and the additional NO was converted from NO$_2$. NO increased rapidly in the first 30 min, reached a maximum of 246 ppm at 180 min and dominated the NO$_x$ emission before 280 min operation. Additionally, the NO$_x$ in the influent was predominated by NO$_2$ after 360-min operation, since the capability of NO$_2$ adsorption of AC reduced. An approach of the influent NO$_x$ of 280 ppm and effluent NO$_x$ of 286 ppm at 600 min indicates that after the time, the carbon had been nearly saturated with NO$_2$ and the conversion capability of NO$_2$ to NO of the carbon was nearly diminished. The effluent gas had a NO$_x$ of 282 ppm at the end (720 min) of the adsorption operation. Our finding of NO$_2$/NO adsorption/ desorption phenomenon is similar to those observed in the study on AC treatment at 50°C for NO$_2$, presented by Gao *et al.* (2011). The mechanism has been reported as follows Eqs. (1)–(6) and Fig. 4 (Gao *et al.*, 2011):
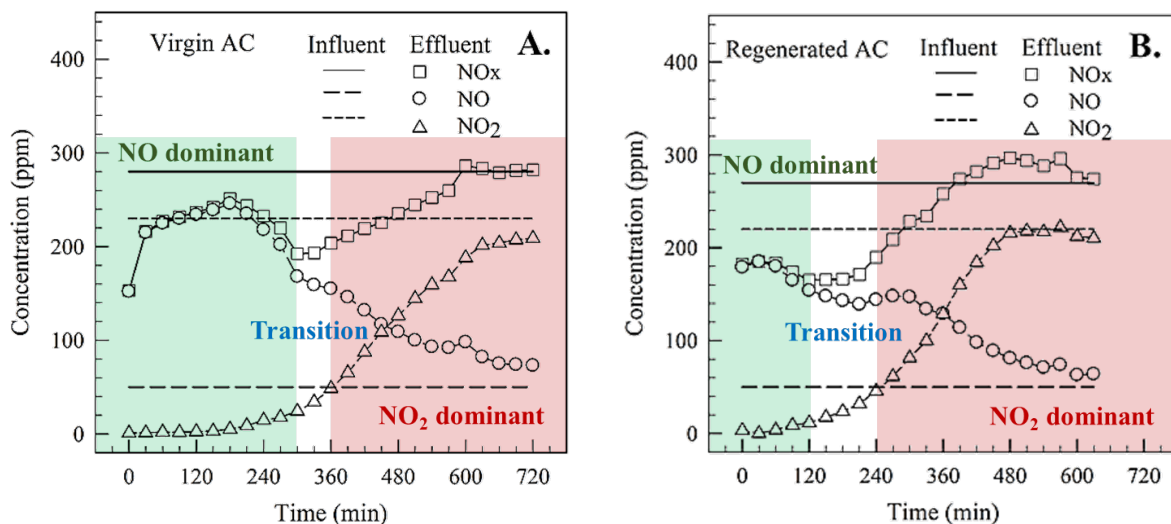
Fig. 2. Time variations of influent and effluent NO_x ($NO + NO_2$), NO, and NO_2 concentrations to and from the (A) virgin AC and (B) regenerated AC columns.
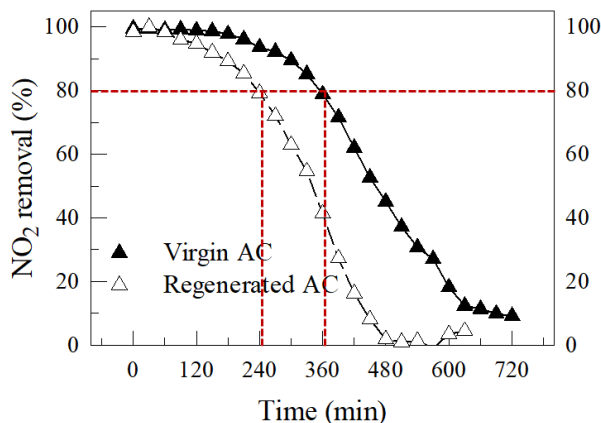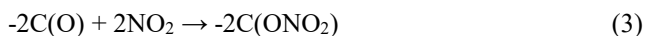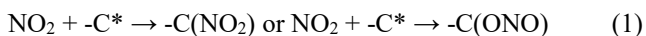

Fig. 3. Time variations of NO_2 removal by the AC.

$$NO_2 + \text{-C*} \rightarrow \text{-C}(NO_2) \text{ or } NO_2 + \text{-C*} \rightarrow \text{-C}(ONO) \quad (1)$$

$$\text{-C}(NO_2) \rightarrow \text{-C}(O) + NO \quad (2)$$

$$\text{-2C}(O) + 2NO_2 \rightarrow \text{-2C}(ONO_2) \quad (3)$$

$$\text{-2C}(ONO_2) + 2NO_2 \rightarrow \text{-2C}(ONO_3) + 2NO \quad (4)$$

$$\text{-C}(NO_2) + \text{-C}(NO_2) \rightarrow \text{-C}_2(ONO_2) + NO \quad (5)$$

$$\text{-C}_2(ONO_2) \rightarrow 2 \text{ -C}(O) + NO \quad (6)$$

The NO_2 could be directly adsorbed/desorbed by functional group "-C*" as Eq. (1), while the stability of adsorbed structure, -C(ONO), was not stable and tend to broken down and release one molecule of NO and form one -C(O) group (as shown in Eq. (2)). Additionally, the functional -C(O) could bind two NO_2 and temporarily form two groups of -2C(ONO$_2$) (as shown in Eq. (3)). Furthermore, the C(ONO$_2$) groups might temporarily react with extra NO_2 molecule and

form a more stable functional group, -C(ONO$_3$) as shown in Eq. (4). On the other hand, the Eq. (5) indicates that two adjacent -C(NO$_2$) groups could be combined and converted to a stable -C$_2$(ONO$_2$), and one molecule of NO would escape from the AC surface. Eq. (6) reports that of -C$_2$(ONO$_2$) could be decomposed and formed -C(O) and NO, when the carbon is thermally regenerated.

Fig. 2(B) shows time variations of NO_2, NO and NO_x concentrations of the gases to and from the bed packed with the regenerated AC. At the start of adsorption, effluent gas had a NO concentration of 180 ppm and in which the additional 130 ppm was converted from the adsorbed NO_2 according to Eqs. (1) and (2). However, during the initial 90 min, there was less than 10 ppm NO_2 emitted from the bed, representing over 90% removal efficiency (as shown in Fig. 3), and most NO_x was in the form of NO. Afterwards, NO_2 increased nearly exponentially and NO decreased nearly linearly with time. At the time of 360 min, rates of NO_2 increase, NO decrease as well as the influent and effluent NO_x were nearly equal. After 480 min, the bed lost its performance for NO_2 removal.

NO$_2$ Adsorptive Removal Performances

By the data shown in Figs. 2 and 3 show time variations of NO_2 removal by the virgin and regenerated AC. The removal is defined by subtracting the effluent NO_2 concentration from the influent one and divided by the influent value. The S-shape profiles demonstrate that the adsorptive NO_2 removal decreased from 100% slowly to around 80% during the beginning period which lasted about 50% of the breakthrough time for both adsorption operations. The phenomena are typical for mass transfer of pollutant(s) to the carbon surface with the fluid flowing through the carbon column. For the column with a packing height of 2.0 cm or 0.75 g of the virgin AC, 50% of the packed AC has a capacity of removing 80–100% or around 90% of the influent NO_2. For the adsorption test with the virgin AC, it was estimated that during the initial 360 min (removal efficiency > 20%) of the adsorption
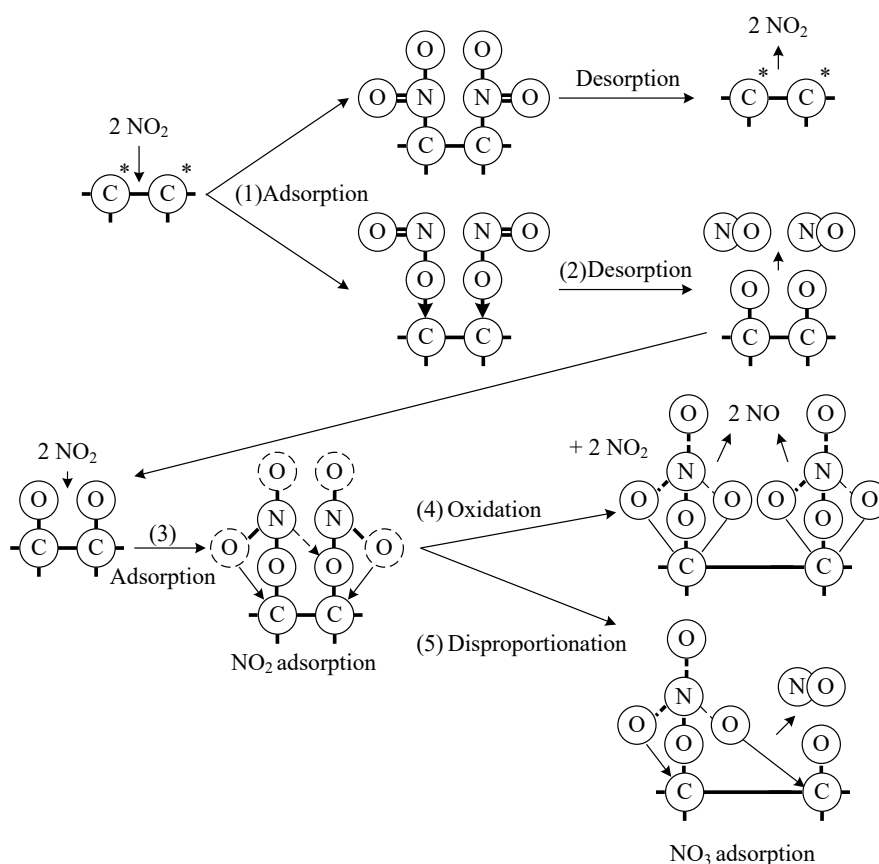
Fig. 4. Adsorption and desorption mechanism of NO_2 by AC bed.

time, the total influent NO_2 was 93.3 mg (= 0.6 L min^{-1} × 360 min × 220 ppm × 0.001 m^3 L^{-1} × 46 (mg m^{-3})/24.5 ppm). There were 90% of NO_2 (84.0 mg) adsorbed. From the data, the adsorptive removal capacity of NO_2 by the virgin AC was estimated to be 224 mg g-AC^{-1}. Table 2 shows that the superficial velocity for the gas flowing through the column cross-sectional area was 0.127 m s^{-1} and by this velocity, the length of mass-transfer zone for the removal of 80% of the influent NO_2 could be estimated to be 0.5 cm.

Similarly, for the regenerated AC with a packing height of 1.7 cm, it was estimated that during the initial 240 min (removal efficiency > 20%) of the adsorption time, the total influent NO_2 was 59.5 mg (= 0.6 L min^{-1} × 240 min × 220 ppm × 0.001 m^3 L^{-1} × 46 (mg m^{-3})/24.5 ppm). Fortunately, the 90% in average (53.6 mg) could be still removed by regenerated AC bed in certain time (240 min) period before breakthrough. The adsorptive removal capacity of NO_2 by the regenerated AC was 155 mg g-AC^{-1}. The regenerated AC has a capacity of about 70% as compared with the virgin one. Bazan *et al.* (2016) used carbonaceous adsorbents obtained from the residue after supercritical extraction of marigold subjected to physical activation and used as nitrogen dioxide adsorbents. Dry air with 1,000 ppm of NO_2 was passed through a column packed with the adsorbents. Results showed that the most effective adsorbent in dry conditions had a NO_2 sorption capacity of 29.2 mg g^{-1}. The capacity was far less the that obtained by the present study.

Take the whole packed AC mass, Fig. 5 shows time

variations of NO_2 adsorptive removal capacity of both AC. Calculate capacity by dividing the cumulative mass of removed NO_2 by the total filled AC mass. The virgin AC had an equilibrium capacity of around 157 mg NO_2 g^{-1} AC with the adsorption time approaching 600 min. The regenerated one had a saturation value of 113 mg NO_2 g^{-1} AC with time approaching 420 min. As a comparison, the regenerated one had a capacity and saturation time of both 70% from the experimental data shown in Fig. 5.

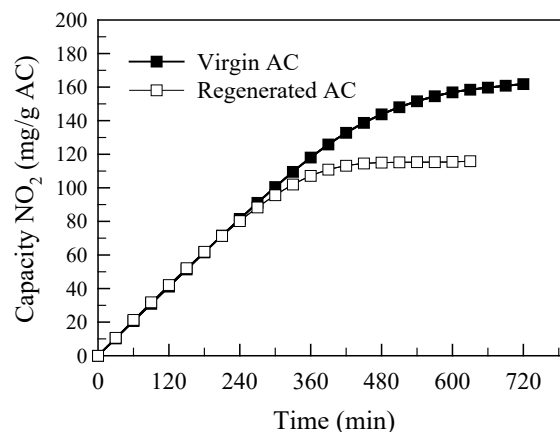Eqs. (2), 4, and (5) display that NO can be produced from

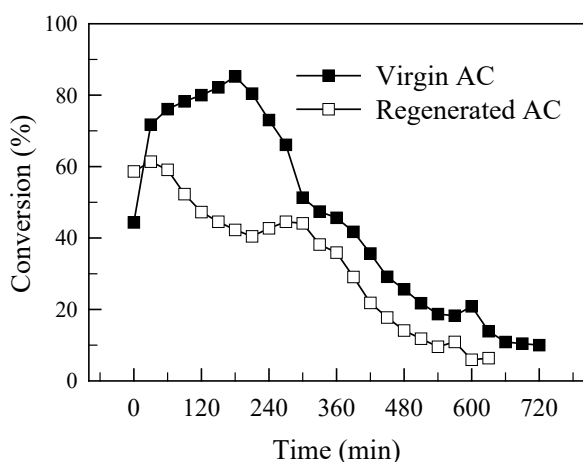**Fig. 5.** Time variations of the adsorptive removal capacity of NO_2 by the AC.

Fig. 6. Time variations of conversion of NO_2 to NO by the AC.

the adsorptive removal of NO_2 as illustrated in Fig. 2. Time variations of conversion of NO_2 to NO by the AC were shown in Fig. 6. The conversion was calculated by dividing the NO increase (ppm) of the effluent gas by the influent NO_2 concentration (220 and 230 ppm for the test with virgin and regenerated AC, respectively). At the start of operation by using the virgin AC, the conversion was 44% and increased to a maximum of 85% in 180 min and decreased finally to about 10% at 720 min. By the regenerated AC, the conversion was 60% at the start and decreased with time to about 5% at 630 min. By the virgin AC, the new carbon had a greater ability to adsorb NO_2 to form "$-C(NO_2)$", when only a part of them converted to NO and desorbed to the effluent gas. At around 180 min, it could be postulated that reactions (2), (4) and (5) dominated with NO converted from the decomposition of $-C(NO_2)$ and $-C_2(ONO_2)$. After the time, there was no enough surface area available for effective adsorption of NO_2 and its conversion to NO thus reduced. For the regenerated AC, effective adsorption of NO_2 and its conversion to NO occurred in the initial 60 min. However, the AC could not convert the adsorbed NO_2 to $-C(NO_2)$, while the conversion reduced gradually until the end of operation.

Characteristics of AC

The chemical regeneration method could only recover 70% of NO_2 adsorptive removal capacity. This loss could attribute to changes in specific surface area, pore volume, and oxygen content in AC material before and after adsorption (as shown in Table 3). The specific surface areas of the virgin-unused and -saturated AC were 676 and 256 and $m^2\ g^{-1}$, respectively. The 62% [= (676–256)/676 × 100%] reduction of surface area could be occupied by the oxidizing substances,

such as $-C(O)$, $-C(ONO_2)$ and $-C_2(ONO_2)$, produced by NO_2 adsorption processes. After the washing regeneration process, the specific surface area of the regenerated AC was recovered to 551 $m^2\ g^{-1}$ and reduced to 235 $m^2\ g^{-1}$ after the NO_2 saturated adsorption. The specific surface area differences between unused and saturated AC was 316 $m^2\ g^{-1}$ (= 57% of the initial value. The ratio of 316/420 or 75% of the avail surface area of the virgin and the regenerated AC is near 70% which corresponds to the ratios of capacity and saturation time as discussed in the preceding paragraph. From the results, it could be postulated that around 57–62 or 60% of the total surface area were available and responsible for processing raw and regenerative AC.

The oxygen contents of the virgin AC increased from 3.79 to 5.09 wt.% after adsorption, and the increase was 1.30 wt.% which might be attributed by the adsorbed oxygen-containing species as cited in Eqs. (2)–(4). The regeneration reduced the oxygen contents from 5.09 to 3.12 wt.%, however, the regenerated AC did not restore its original performance due to pores and surface area volume reduction as shown in Table 3. The oxygen content of the regenerated AC after adsorption increased to 6.21 wt.%.

Table 3 also lists pore volume of the virgin and regenerated AC before and after adsorption. Pore volume of the virgin AC reduced from 0.326 to 0.124 $cm^3\ g^{-1}$ after adsorption, and the decrease was 0.202 $cm^3\ g^{-1}$. For the regenerated AC, The reduction before and after adsorption was 0.154 $cm^3\ g^{-1}$, 0.262 and 0.108 $cm^3\ g^{-1}$, respectively. The ratio of 0.154/0.202 or 76% of the pore volume decrease is near 70% which corresponds to the ratios of capacity and saturation time as discussed in the proceeding section. Fig. 7 shows pore volume distributions of the virgin and regenerated AC. For the virgin AC, most pores had sizes between 1.1 to 2.5 nm and the volume reduction occurred mainly in the same pore size range. The regenerated AC had similar pore size as the virgin one, however, the reduction in pore volume occurred mainly in the size range of 1.1–1.5 nm.

Regeneration Leachate

Table 4 shows properties of aqueous solution leached from AC regeneration. Aqueous solution from the first leaching operation by alkaline water adjusted to pH 10 turned to acidic with a pH of 2.36. The leachate from the second leaching operation by pure water was also acidic with a pH of 3.77. Nitrate was the only anion detected in both leachates. Gao *et al.* (2011) states that the adsorbed NO_2 might converted into an adsorbed form of nitrate as $-C_2(ONO_2)$. Upon leaching, $-C_2(ONO_2)$ hydrolyzed to aqueous nitrate and the corresponding equation might be expressed as:
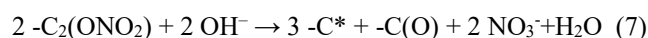
$$2\ \text{-}C_2(ONO_2) + 2\ OH^- \rightarrow 3\ \text{-}C^* + \text{-}C(O) + 2\ NO_3^- + H_2O \quad (7)$$

Table 3. BET surface area, pore volume, and oxygen content of AC.

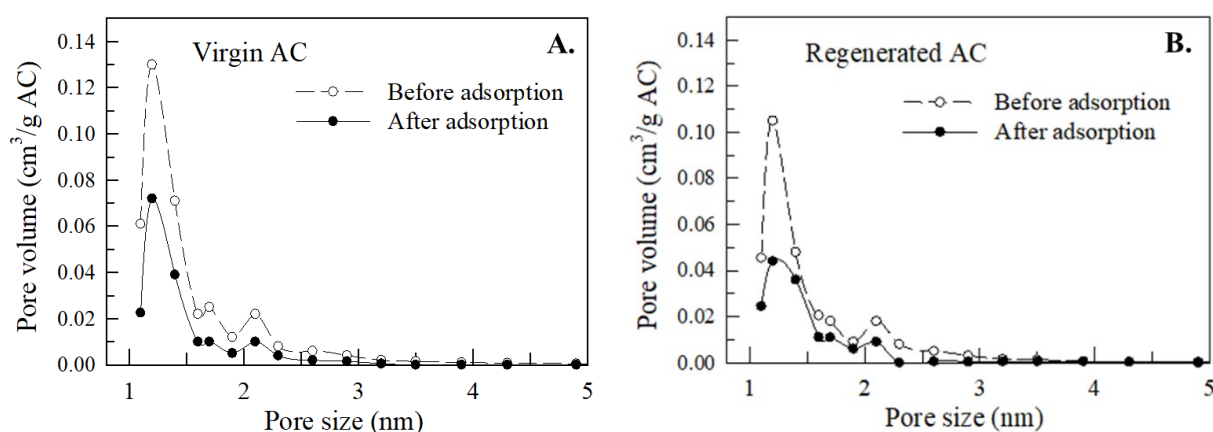| Activated Carbon Columns	Oxygen content, wt.%	Surface area, $m^2\ g^{-1}$	Pore volume, $cm^3\ g^{-1}$
Virgin	3.79	676	0.326
Virgin after adsorption	5.09	256	0.124
Regenerated	3.12	551	0.262
Regenerated after adsorption	6.21	235	0.108

Fig. 7. Pore volume distributions of the (A) virgin AC and (B) regenerated AC.

Table 4. Properties of aqueous solution leached from AC regeneration.

Liquid for regeneration	Leached water from AC regeneration	
	NO_3^- (mg L^{-1})	pH
Alkaline water	624	2.36
Pure water	25.7	3.77

$$2 \text{ -}C_2(ONO_2) + H_2O \rightarrow 3 \text{ -}C^* + \text{-}C(O) + 2 \text{ } HNO_3 \qquad (8)$$
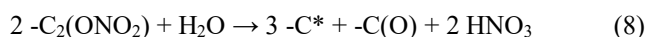
Eqs. (7) and (8) demonstrate that the adsorption site "-C*" could be regenerated by leaching the adsorbed AC by alkaline solution or water, and oxygen contents of the AC could be reduced.

CONCLUSIONS

In this study, passing the test air stream containing 230 ± 10 ppm NO_2 and 50 ppm nitric oxide (NO) through an activated carbon-packed bed for the purpose of studying the adsorptive conversion behavior of NO_2 by the activated carbon (AC) at room temperature. The regenerated carbon was regenerated by washing with a water and caustic solution, and dried to carry out repeated adsorption tests. The following conclusions can be drawn:

1. At the beginning of adsorption, two nitrogen dioxide molecules combined with two adjacent -C* (or -OC group) to from -C(NO_2) or -C(ONO_2), and release molecules of NO from the AC surface. The adjacent group of -C(NO_2) could further form -C$_2$(ONO_2) and enhance the stability of adsorbed NO_2.
2. The net adsorptive conversion removal capacity of NO_2 by the virgin AC and regenerated AC was 224 and 155 mg g^{-1} AC, respectively, during the initial 50% of the breakthrough time. For the whole breakthrough time, the virgin AC had an equilibrium capacity of around 157 and 113 mg NO_2 g^{-1} AC.
3. Regeneration restored around 70–75% of effective surface area, pore volume, and adsorptive conversion capacity of the virgin AC. Leached caustic solution obtained from the carbon regeneration contained only nitrate and the phenomena indicates the adsorbed -C$_2$(ONO_2) hydrolyzed following the equation $2 \text{ -}C_2(ONO_2) + H_2O$ $\rightarrow 3 \text{ -}C^* + \text{-}C(O) + 2 \text{ } HNO_3$.
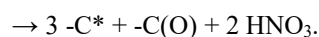
The positive results of NO_2 removal by AC column found in the current study promote the development of the real-scale equipment and need to confirm its durability. The operation and phenomenon would be significantly different in a scale-up progress for a more practical use. The real-scale equipment could include twin beds, one in operation and the other in regeneration. A regeneration process will include (1) caustic desorption of the adsorbed NO_2 and NO_3, (2) water rinsing of the regenerated carbon, and (3) drying of the rinsed carbon.

NOMENCLATURES

-C*: active site on the carbon surface.
-C(O): oxygenated carbon surface.

REFERENCES

Bazan, A., Nowicki, P. and Pietrzak, R. (2016). Removal of NO_2 by carbonaceous adsorbents obtained from residue after supercritical extraction of marigold. *Adsorption* 22: 465–471.

Chen, L., Lin, J.W. and Yang, C.L. (2002). Absorption of NO_2 in a packed tower with Na_2SO_3 aqueous solution. *Environ. Prog. Sustainable Energy* 21: 225–230.

Chen, L., Lin, K.F. and Yang, C.L. (2011). Pilot study of absorption of NO_2 with Na_2S aqueous solutions. *Environ. Prog. Sustainable Energy* 30: 632–639.

Chen, Y., Wang, M., Du, X., Ran, J., Li, Z. and Tang, D. (2018). High resistance to Na poisoning of the V_2O_5-Ce$(SO_4)_2$/TiO_2 catalyst for the NO SCR reaction. *Aerosol Air Qual. Res.* 18: 2948–2955.

Curtin, T. (2005). Selective catalytic reduction of NO_x. In *Environmental catalysis*, Grassian, V.H. (Ed.), CRC Press, Boca Raton, pp. 197–210.

Du, W., Zhang, Y., Chen, Y., Xu, L., Chen, J., Deng, J., Hong, Y. and Xiao, H. (2017). Chemical characterization and source apportionment of $PM_{2.5}$ during spring and winter in the Yangtze River Delta, China. *Aerosol Air Qual. Res.* 17: 2165–2180.

Fang, C., Zhang, Z., Jin, M., Zou, P. and Wang, J. (2017). Pollution characteristics of $PM_{2.5}$ Aerosol during haze periods in Changchun, China. *Aerosol Air Qual. Res.* 17: 888–895.

Gao, X. Guo, R.T. Ding, H.L. Luo, Z.Y. and Cen, K.F. (2009). Absorption of NO_2 into Na_2S solution in a stirred tank reactor. *J. Zhejiang Univ. Sci. A* 10: 434–438.

Gao, X., Liu, S., Zhang, Y., Luo, Z., Ni, M. and Cen, K. (2011). Adsorption and reduction of NO_2 over activated carbon at low temperature. *Fuel Process. Technol.* 92: 139–146.

Görgülü, A., Koç, Y., Yağlı, H. and Koc, A. (2018). Adsorption of nitrogen dioxide (NO_2) for different gas concentrations, temperatures and relative humidities by using activated carbon filter: An experimental study. *Int. J. Adv. Eng. Res. Sci.* 5: 2349–2456.

Guo, R.T., Pan, W.G., Zhang, X.B., Ren, J.X., Jin, Q. and Xu, H.J. (2012). Absorption of NO_2 into aqueous $(NH_4)_2SO_3$ solution in a stirred tank reactor. *Environ. Prog. Sustainable Energy* 32: 465–469.

Huang, Y., Cao, J.J, Kang, F., You, S.J, Chang, C.W. and Wang, Y.F. (2017). High selectivity of visible-light-driven La-doped TiO_2 photocatalysts for NO removal. *Aerosol Air Qual. Res.* 17: 2555–2565.

Jiang, N., Guo, Y., Wang, Q., Kang, P., Zhang, R. and Tang, X. (2017). Chemical composition characteristics of $PM_{2.5}$ in three cities in Henan, central China. *Aerosol Air Qual. Res*. 17: 2367–2380.

Liu, H.B., Zhang, Z.X., Li, Q., Chen, T.H., Zhang, C.G., Chen, D., Zhu, C.Z. and Jiang, Y. (2017). Novel methods for preparing controllable nanoporous α-Fe_2O_3 and its reactivity to SCR de-NO_x. *Aerosol Air Qual. Res.* 17: 1898–1908.

Persinger, R.L., Poynter, M.G., Ckless, K. and Janssen-Heininger, Y.M. (2002). Molecular mechanisms of nitrogen dioxide induced epithelial injury in the lung. *Mol. Cell. Biochem.* 234–235: 71–80.

Shen, C.H. and Rochelle, G.T. (1998). Nitrogen dioxide absorption and sulfite oxidation in aqueous sulfite. *Environ. Sci. Technol.* 32: 1994–2003.

Shirahama, N., Moon, S.H., Choi, K.H., Enjoji, T., Kawano, S., Korai, Y., Tanoura, M. and Mochida, I. (2002). Mechanistic study on adsorption and reduction of NO_2 over activated carbon fibers. *Carbon* 40: 2605–2611.

U.S. Environmental Protection Agency (U.S. EPA) (1987). Nitrogen dioxide CASRN 10102-44-0. *Chemical Assessment Summary, Integrated Risk Information System (IRIS)*, National Center for Environmental Assessment.

Wang, Y., Cheng, K., Tian, H.Z., Yi, P. and Xue, Z.G. (2018). Analysis of reduction potential of primary air pollutant emissions from coking industry in China. *Aerosol Air Qual. Res.* 18: 533–541.

Wu, C.Y. and Chou, M.S. (2014). Reduction of nitrogen dioxide from etching vent gases by scrubbing with caustic sodium sulfide solution. *J. Chem. Technol. Biotechnol.* 89: 1850–1858.

Xu, J.Y., Jiang, H., Zhao, H.R. and Stephens, B. (2017). Mobile monitoring of personal NO_x exposures during scripted daily activities in Chicago, IL. *Aerosol Air Qual. Res.* 17: 1999–2009.

Zhang, W.J., Bagreev, A. and Rasouli, F. (2008). Reaction of NO_2 with activated carbon at ambient temperature. *Ind. Eng. Chem. Res.* 47: 4358–4362.

Zhang, X., Kang, J., Chen, H., Yao, M. and Wang, J. (2017). $PM_{2.5}$ meets blood: In vivo damages and immune defense. *Aerosol Air Qual. Res.* 18: 456–470.